Polish Journal of Environmental Studies Vol. 7, No. 5 (1998), 257-266

Review

Speciation Analysis of Chromium in Waters

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Received 12 March, 1998
Accepted 10 July, 1998

Abstract

The total content of chromium in natural waters does not generally exceed several µg/l. Thus, it is obvious that various forms of chromium will occur at the levels of tenths or hundredths of µg/l. Their determination requires the application of a sufficiently sensitive method, but its specificity has an important role to play in the case of chemical individuals or selectivity in regard to speciation of a group of compounds, e.g. valency states or organic chromium complexes.

Generally, however, there is a lack of specific and selective methods, and the concentrations of various forms of the analyte occur often at the level of detection limits of even such sensitive techniques as atomic absorption spectrometry. This paper presents a review of currently available analytical possibilities of chromium speciation investigations in natural water samples. Analytical procedure schemes enabling "total speciation analysis" have been discussed in some detail. A large group of methods used in the speciation analysis of chromium(III) and chromium(VI), both in off-line and on-line mode, has also been discussed.

Keywords: Water, chromium speciation, speciation analysis.

Introduction

The chromium content in surface waters is usually at the low µg/l level, typically between 0.3 and 6 µg/l. Comparable chromium contents can be found in ground waters. The mean chromium concentrations in Polish rivers do not exceed 5 µg/l. High concentrations of chromium are occasionally present in surface waters of some rivers in the Odra drainage basin e.g. the Bobr: 1522 µg/l, the Nysa Luzycka: 846 µg/l, the Nysa Ktodzka: 89 µg/l and are of natural origin (due to penetration of chromium-rich basal rocks by waters). Chromium anthropogenic anomalies in surface waters are known to occur in the Warta (161 µg/l), in the Radomka (47 µg/l) and in the Bzura (242 µg/l) drainage basins. However, the mean concentration of chromium in surface waters of these rivers is also less than 5 µg/l [1]. Similar chromium concentrations have been found in the following rivers in Europe: the Rhine (Germany) 4.2 + 26 µg/l, the Clyde (Scotland) 10 + 45 µg/l, the Danube (Austria) 0.4 + 1 µg/l, the Thames (England) n.d. H-30 µg/l [2], and in the North American rivers: the Upper Mississippi 0 + 40 µg/l, the Upper Colorado 0 + 90 µg/l; on the average 6 µg/l in clean waters and 50 µg/l in contaminated waters [3]. The chromium content in drinking water in Poland ranges from 0.07 µg/l to 2 µg/l, while in the USA the content is much higher - from 0.1 µg/l to 35 µg/l. Chromium concentration in sea water is one order of magnitude lower than in surface waters, typical concentrations being 0.1 + 0.5 µg/l [4].

The concentrations quoted above reflect only the total chromium content comprising a rich variety of chemical and physical species. These different chemical species have different reactivities and effects. The availability of chromium species to organisms as well as toxic effects strongly depend on chromium species. Whereas chromium(III) is considered essential for the maintenance of glucose, lipid and protein metabolism, chromium(VI) is reported to be toxic and may also be carcinogenic, owing to its oxidizing potential and easy permeation of biological membranes. Transport of chromium in natural waters and between different compartments in the environment also depends on a kind of chromium species. For instance, sedimentation, the primary removal process of dissolved chromium species from lake, river or sea water, can occur only if they are bound to a particulate phase. Thus, the distribution of chromium species is an important factor for the fate of this metal in the environment [3, 5, 6].

Speciation of metals, which is understood as specifying the different, defined species, forms or phases in which the element occurs in the environment, is the key to the study

of behaviour and fate of metals, in this case chromium, in the environment. By applying experimental techniques, it is possible to distinguish within the total concentration:

- chemical species or metal compounds, which are desc ribed in terms of well defined chemical stoichiometry (e.g. ions, molecules, complexes);
- chemical fractions, which represent a group of chemi cal forms operationally defined with respect to the separa tion techniques applied. The total metal concentration is distributed also between the dissolved, particulate, and col loidal fractions. Measurements of the chemical forms are usually more readily available than detailed speciation stu dies **[7].**

The Speciation of Chromium in Waters

Chromium can occur in natural waters in a variety of chemical forms, namely as dissolved free aquo-ions, as dissolved complexes with inorganic (mainly hydroxide, sulfate, chloride) and organic ligands (humic and fulvic acids, specific chelators being secretions of organisms and synthetic ligands: NTA, EDTA) and also as particulate (or colloidal) phases or adsorbed on particulate (or colloidal) phases.

According to thermodynamic calculations, inorganic chromium(III) may exist in aqueous solution as hydroxo species, including Cr^{1+}, $Cr(OH)^{2+}$, $Cr(OH)_2^{+}$, $Cr(OH)_3$, $Cr(OH)_4$-, $Cr_2(OH)_2^{4+}$, $Cr_3(OH)_4^{5+}$, and a mixed ligand complex, such as $Cr(OH)Cl^{+}$, $Cr(SO_4)^{+}$. Free aqua cations, hydroxo anions, polynuclear cationic species and chloro and sulfato complexes are ignored because their contribution under typical pH conditions in surface waters is insignificant. $Cr(OH)^{2+}$ predominate at pH ca. 5, whereas $Cr(OH)_3$ prevails at pH ca. 8. Chromium(VI) may be present in aqueous solutions mainly as chromate, dichromate, hydrogen chromate, chromic acid, and hydrogen dichromate. The last two species have been detected only in strongly acidic solutions. In typical surface waters when concentration of chromium is less than 5 µg/l, only $HCrO_4^{-}$ and CrO_4^{2-} can be found. Chromate ion is predominant at pH > 7, while hydrogenchromate is predominant at pH < 6 [8, 9].

Thermodynamic calculations have also shown that chromium exists almost exclusively as hexavalent in oxygenated sea water at pH = 8 [10]. These theoretical predictions are, however, contradicted by analytical studies that have revealed the further existence of chromium(III), obviously as $Cr(OH)_2^{+}$, and as organically bound forms and colloidally sorbed species. The kinetic inertness of chromium(III) complexes appears to stabilize the chromium(III) fraction, which increases with the content of organic substances and in anoxic zones [10].

In comparison to oceans, river waters tend to have lower dissolved solids, and higher particulate loads, higher biological activity and very transient transport and can be influenced more readily by inputs from industrial and municipal sources. As a result, at lower pH 5-7 and in the presence of readily reducible organic substances, chromium(III) species are predominant chromium forms in surface waters. Investigation results presenting a different distribution of chromium species in lake waters have been published in [11, **12].**

Thermodynamic calculations are useful in order to predict the speciation of chromium in natural waters, using known concentrations of ligands and compilations of stability constants. This approach is especially useful for the inorganic ligands, for which the concentrations in various systems are easily determined and the stability constants are available in most cases. It is much more difficult to use this approach for organic ligands, although the stability constants of a large number of complexes with simple organic ligands are available. The concentrations of the prevailing number of various organic compounds in natural waters are, however, in most cases unknown. Complexation of metal ions with humic and fulvic acids cannot be defined with simple stability constants due to the polyelectrolytic character of these compounds. Surface complexation constants for binding of chromium species to the surface of oxides are available in only some cases. Formation of solid phases can be evaluated from the solubility products [13].

Such calculations give only an incomplete and simplified picture that does not include the organic complexation and chromium bound to a particulate phase.

Thus, the evaluation of speciation based on thermodynamic data should be complemented by an experimental approach in order to obtain a more detailed picture of speciation. Therefore, there is a need to have analytical possibilities to distinguish between the various solute and adsorbed species or to identify the solid or surface sites (organic surface, organically coated particles, iron(III) oxide, and aluminium silicates) in which the metal ion is present or bound to. Usually, the evidence for a particular form of occurrence is incomplete and difficult to obtain. The analytical task is more complex, because individual chemical species are often present at nano- and picomolar concentrations.

There are only a few analytical techniques available that have sufficient sensitivity and selectivity for the direct determination and speciation of ultratrace levels of chromium in water. Sample pre-treatment techniques, which include analyte element separation and preconcentration, are required in order to determine the low levels of the individual chromium species even when the most sensitive techniques, such as electrothermal atomic absorption spectrometry (ET-AAS), are used. Even though other analytical techniques such as inductively coupled plasma atomic spectrometry (ICP), neutron-activation analysis, electrochemical methods or X-ray fluorescence have been used for this purpose, AAS being a highly selective and specific element technique is ideally suited as a detector for speciation analysis [14].

Based on Hulanicki [15, 16], the process leading to a quantitative evaluation of the contents of various forms of the analyte has been described in this paper as speciation analysis.

Analytical Methods

The presentation of the techniques used in the speciation analysis of chromium calls for a certain ordering of the research done so far. This author does not aim at a comprehensive discussion of the problem. He would just like to mention certain trends, review the most important achievements of recent years and attempt to classify them. As far as the classification is concerned, there are a number of possibilities. There is no doubt that the traditional classifi-

cation based on the analytical methods used is interesting. The character of the speciation analysis of chromium, according to chemical species, valency states and operationally defined forms, also might serve as a basis for classification. The methods of speciation analysis of chromium may be divided into direct ones and those requiring sample pretreatment. It is quite tempting to classify, according to sophistication levels, the methods where one of the reference points may be approaches to separation, enrichment and determination techniques in off-line mode, and the other - fully automated FTA systems combining sample pretreatment on-line with detection methods.

This paper concentrates on the more important publications suggesting comprehensive analytical methods ("total" speciation analysis) and a numerous group of methods restricting the speciation analysis of chromium to the determination of its valency states. All the procedures have been classified according to the degree of their sophistication. The former methods are a suitable tool for the study of environmental chemistry of chromium; and the latter are used predominantly to determine the toxicity of the environment caused by chromium compounds.

"Total" Speciation Analysis of Chromium

The "'total" speciation analysis of chromium in waters going far beyond simple operational procedures consisting in the determination of dissolved and particulate chromium is currently a very distant aim. The available methods make it possible to determine only a few forms of dissolved chromium. Generally, they require not only separation of the analyte forms being determined but also their preconcentration. Precipitation methods (coprecipitation and collection) are often used for this purpose. Coprecipitation is an established technique for preconcentration which can be performed with standard laboratory equipment.

One of the earlier discussions of such an approach to chromium speciation can be found in Nakayama et al. [17]. The principle of their method is based on the fact that only chromium(III) is recovered by Fe(III)-hydroxide, and both chromium(III) and chromium(VI) are collected by Bi(I-II)-hydroxide. In order to quantitatively collect chromium(III) and both chromium(III/VI) together, Fe(III)-hydroxide and Bi(III)- hydroxide were added, respectively, to two suitable volumes of sea water (pH = 8). The best way of collecting the organic chromium species appeared to be decomposition to inorganic chromium(III) or chromium(VI) species (heating acidified sample with ammonium persulfate) followed by collection using Bi(III)-hydroxide. After 24 h the precipitates were dissolved in hydrochloric acid and were extracted with a p-xyle-ne solution containing triisooctylamine to remove iron and bismuth which give an interference in the GF-AAS method. The method of speciation analysis allows determination of inorganic chromium(III), a sum of inorganic chromium(III/VI), and the total of chromium. The standard deviations were 5.8, 2.4 and 5.1%, respectively. Chromium(VI) and organically-bound chromium were calculated by the difference. In their work, the authors found that the average total concentration of the dissolved chromium was 0.5 µg/l (the Sea of Japan and the Pacific Ocean), consisting of 10 ÷ 20% inorganic chromium(III), 25 ÷ 40% chromium(VI) and 45 ÷ 60% organic chromium species.

Less time-consuming chromium speciation procedures are also known. A speciation analysis of chromium by coprecipitation with lead salts has been described by Obiols et al. [18]. It allows the partitioning of the total concentration of the metal into four fractions: chromium(VI), free chromium(III), complexed chromium(III), and particulate chromium. Complexed chromium corresponds to the term organic chromium species used in [17]. The speciation analysis scheme was based on four independent processes. The particulate chromium was separated from water by filtering through a 0.45 µm membrane filter; filters were treated with diluted nitric acid to dissolve and then chromium was determined. The other three chromium species were determined in a filtrate. Chromium(VI) was separated by coprecipitation with lead sulphate as lead chromate. The reaction was carried out in an acidified sample at pH 3 using lead nitrate and ammonium sulphate solutions. Coprecipitation with lead phosphate(II) made it possible to determine total chromium(VI) and free chromium(III) as chromium(III) phosphate and lead(II) chromate(VI), respectively. In this case ammonium phosphate was used to precipitate lead salts at pH 6. Both precipitates were dissolved in concentrated nitric acid. Concentrations of chromium in both fractions and total concentration of the dissolved chromium were measured by means of GF-AAS. The detection limits for the dissolved chromium, chromium(VI), total chromium(III/VI), and particulate chromium were: 0.06 µg/l, 0.05 µg/l, 0.13 µg/l and 0.22 µg/l, respectively; the precision was in the range of 1.9 ÷ 9.3%. Total concentrations of chromium in the waters being investigated ranged from 1.9 µg/l to 4.7 mg/1, including the dissolved chromium in the amount of 0.5 µg/l to 69 µg/l. Chromium(VI) constituted 10 ÷ 30%, free chromium(III) 25 ÷ 90% and complexed chromium 6 ÷ 50%.

Johnson [19] measured the chromium(III), chromium(VI), and total dissolved chromium concentrations, and calculated the colloidal/organic chromium fraction by the difference. The analytical procedure involved the use of ion-exchange columns. Extraction columns containing the polar phase aromatic sulphonic acid silane (Baker) were used for the collection of chromium(III), and anion exchanger Bio-Rad 1-X4 for the selective preconcentration of chromate. Water samples were acidified, passed through membrane filters (0.45 µm.) and then through ion-exchange columns. The columns were eluted with 5.0 M HNO_3 and 1.0 M NH_4NO_3 + 0.1 M $HN0_3$ for chromium(VI) and chromium(III), respectively. The concentrations of both chromium species were determined by means of the GF-AAS method. Total chromium was analyzed as chromium(III) after transforming chromium(VI) and the colloidal/organic chromium fraction to dissolved chromium(III). The detection limits were 0.019 µg/l for chromium(VI) and 0.20 µg/l for chromium(III) (for a 200 ml sample).

Hiraide and Mizuike [20] described a method that can be used to actually isolate and measure the three dissolved forms of chromium. Its improved version has been presented by Beaublen et al. [11]. The separation of individual forms was carried out on an ion-exchange resin. A sample filtered through a 0.4 µm filter after pH adjustment at 4.7 was passed through a column with an anion-exchange resin Sephadex DEAE A-25. The anionic chromium(VI) and negatively charged colloidal/organic chromium were retained on the resin while the cationic forms of chromium(III) were present in the eluent. Then the drained resin was treated

with hydroxylamine hydrochloride to reductively elute the resin-bound chromium(VI). Three separate water washings allow to obtain a cumulative recovery of 94.3%. It was found that the reduction recovery occurs due to the reduction of resin-bound chromium(VI) in acetate buffer medium and the subsequent precipitation of chromium(III) oxyhydroxides. This problem can be avoided if reductive elution is carried out immediately. Then the column was eluted with 4 M HNO_3 in order to release residual chromium (all negatively charged colloidal and organic chromium species). Particulate chromium concentrations were calculated as the difference between the acid-leachable (pH 1.6) and total dissolved concentrations. Chromium species concentrations in every fraction/eluent were determined by means of GF-AAS with Zeeman background correction. The method of chromium speciation described enables determination of three forms of chromium dissolved in freshwater, with detection limits of 21 ng/1 for chromium(III), 4 ng/1 for chromium(VI), and 8 ng/1 for colloidal/organic chromium. The significant differences in the detection limits are justified by the procedure used; both chromium(VI) and colloidal/organic chromium were separated and preconcentrated before determination, only chromium(III) was measured directly after separation. The method is selective for either chromium(III) or chromium(VI) in the concentration range of 83 ÷ 500 ng/1, even when one species is in excess. Average concentrations of total dissolved chromium in the epilimnetic waters of the Great Lakes were found to be from 69 ng/1 to 351 ng/1, chromium(VI) made up 75 ÷ 85% and colloidal/organic form about 10% of the dissolved chromium, chromium(III) was consistently below the analytical detection limit.

This short review of the most sophisticated procedures of chromium speciation analysis presents the existing possibilities for the determination of chromium species in water environments. After separating and determining total chromium in suspension, it is possible to determine chromium(VI) corresponding to the presence of dissolved chromates, and two forms of chromium(III) as inorganic and organic complexes. Using thermodynamic calculation results, inorganic complexes can be defined most likely as cationic aquahydroxycomplexes; however, organic complexes, always indirectly determined, are a typical operationally defined species; for example Nakayama et al. [21] defined organic chromium as the species which is not coprecipitated with metal hydroxides and is recovered after digesting a sample solution. This is based only on the fact that some water-soluble chromium chelates are not coprecipitated with hydroxides. The existence of this species as organic chromium has not been verified.

Determination of Valency States

There is a rapidly increasing demand for fast and reliable analytical methods for the determination of valency state of chromium in tap water, surface waters, and waste waters. As mentioned before, the interest in chromium is governed by the fact that its toxicity depends critically on its oxidation state. The importance of this problem becomes evident when we study recent publications. The majority of papers deal exclusively with the speciation analysis of chromium valency states.

Some of these methods involve the separation (and sometimes preconcentration) of one inorganic form and the calculation of the concentration of the other form by the difference between total dissolved chromium and the measured species. The methods that make it possible to directly measure chromium(VI) are more valuable due to its definitely more toxic properties. The procedures consisting in simultaneous or parallel determination of chromium(III) and chromium(VI) are less often used.

The methods of analysis of chromium(III) and chromium(VI) usually develop into two steps: separation of one or both of the considered species from the original matrix, and then determination of each of them. A great variety of separation techniques have been utilized, including the use of chelating and ion-exchange resins, the chelation-extraction with organic solvents, and the techniques of coprecipitation.

These approaches assume that no other species contribute significantly to the observed total concentration, i.e. that phases such as chromium complexed or adsorbed to various organic ligands and/or colloids (colloidal/organic chromium) do not exist.

The application of chromium valency state determination to a routine analysis of environmental samples has led to the development of fully automated analyzers comprising combined techniques being used alongside the traditional methods of speciation analysis with separation and preconcentration in the off-line mode.

Direct Speciation Analysis

There have been not many publications describing direct speciation analysis. Giving up preconcentration and separation of chromium species in the case of water samples is possible only if a specific or highly selective analytical method with an adequate detection limit is available. The requirements can surely be met by numerous modifications of a well-known and widely used spectrophotometric method of chromium(VI) determination with diphenylcarbohydrazide [22, 23].

Another interesting suggestion is the work of Kabasakalis [24], in which the author described a method of chromium(VI) determination in the presence of chromium(III) without pre-separation of the two states. This method is based on the fluorescence produced from the ion-association complex between the crystal violet cation and the iodochromate anionic complex (λ_{exc} = 256 nm and λ_{em} = 521 nm). The fluorescence intensity was constant for 10 minutes. The iodochromate complex forms in the presence of 1000-fold excess of iodide over chromium(VI) at pH 2. The detection limit is 0.94 μg/dm^3, and the linear range is up to 60 μg/dm^3 The method is simple, rapid and low cost. The determination of Cr(III) requires an analysis of total chromium by means of a well-known method. The method is useful for the study of chromium speciation in polluted waters.

Chromium(III) and chromium(VI) species can also be determined directly in water using cathodic stripping voltametry (CSV) preceded by adsorptive collection of complex chromium(III) with diethylenetriaminepentaacetic acid (H_2DTPA) on hanging mercury drop electrode. Boussemart at al. [18] adapted the method for the determination of chromium (VI) and total dissolved chromium in sea water. Chromium(VI) originally present in a sample is reduced to

chromium(III) at the electrode surface during deposition at -1.0 V, and subsequently forms a complex with the DTPA which adsorbs on the mercury drop. The peak corresponding to the reduction of the adsorbed complex of chromium(III) appeared at -1.22 V at pH 5.2. The adsorptive complex is also produced when chromium(III) is present in solution. However, the reduction current of the dissolved complex of chromium(III) was not stable. The concentration of chromium(VI) can be determined in the presence of chromium(III) by allowing the sample to react with DTPA for 30 min at pH 6.8 prior to the adsorption step. Under those conditions reactive chromium(III) is converted to electrochemically inert complexes. The different behaviours of chromium(VI) and chromium(III) can also be utilized also to analyze reactive chromium(III) in sea water samples. The reactive chromium(III) concentration is determined by adsorption of the DTPA complexes onto the hanging mercury drop electrode immediately after the DTPA addition to the sea water. The concentration of total chromium(III) (reactive and organically complexed) can then be evaluated by the difference between total chromium and chromium(VI). Total dissolved chromium was determined after UV-irradiation of the sample at its original pH. The pre-treatment procedure was necessary to transform chromium(III) to chromium(VI) and to eliminate natural chelators and surface-active compounds. The limit of detection for chromium(VI) and total chromium in sea water is 5 ng/1 at a deposition time of 2 min. The sensitivity of the CSV procedure for chromium(VI) in sea water is 10 times lower than in freshwater due to major cations, calcium and magnesium, competition for DTPA in the sea water. The method was tested on samples from the Mediterranean, where concentrations of chromium(VI) and chromium(III) were ca. 0.25 µg/l and 0.05 µg/l, respectively. The author's conclusion is as follows - the method was sufficiently sensitive to detect chromium(VI) and total dissolved chromium in sea water samples, but insufficiently sensitive to detect the low levels of chromium(III) occurring in sea water either directly (from the peak height immediately after the reagent addition) or by difference (total chromium minus reactive chromium(VI)) due to the much higher concentrations of chromium(VI).

Speciation Analysis in *off-line* Mode

This group of methods comprises analytical procedures in which the essential process of sample preparation takes place outside the unit used for final determinations.

The routine method, recommended by USEPA (method 218.4), consists in the extraction of chromium(VI) with ammonium pyrrolidinecarbodithioate (APCDT) into methyl isobutyl ketone (MIBK), followed by the determination of chromium in the organic phase using the AAS method [26]. Total chromium is determined in the same way after preliminary oxidation of chromium(III) to chromium(VI).

The shortcomings of using MIBK as a solvent are its relatively high solubility in water, slow phase separation, capability to extract sodium, and the instability of the metal complexes in the solvent. Furthermore, MIBK has wetting properties which make it difficult to use in graphite furnace atomic absorption spectrometry. One solution to this problem is to use a less water-soluble solvent such as chloroform and to back-extract the metal-dithiocarbamate complexes into a nitric acid solution for GF-AAS. The procedure proposed in [27] is derived from this method. Basically, it involves the formation of a chromium(VI) complex with sodium diethyldithiocarbamate, which is then quantitatively extracted from a pH 4.0 ÷ 4.5 solution with chloroform. In that pH range chromium(III) forms stable hexaaquacomplexes which cannot be extracted with chloroform. Another extraction to the water phase is carried out with a mercuric(II) nitrate solution at pH 1.6. Hg(II) replaces chromium bonded in the DDTC complex very efficiently. Chromium is determined directly by the GF-AAS method. Total chromium is determined after oxidation of chromium(III) to chromium(VI). Using a 200 ml water sample, a preconcentration factor of 80 can be obtained, which allows for a chromium analysis at the level of at least 0.01 µg/l, the average recovery is 95%. The extraction procedure provides a much larger concentration factor than the MIBK method and is suitable for chemical speciation studies of chromium in natural water systems.

A similar approach has been described by Siepak in [28]. Total chromium was determined directly in the acidified samples, chromium(VI) in the extracts from those samples. The extraction was performed using ammonium tetramethylenedithiocarbamate and methylisobutylketone in the presence of a phosphate buffer. The determination of chromium was performed using the technique of multiple injection of GF-AAS. Chromium(III) was calculated from the difference between total chromium and chromium(VI).

Speciation of chromium by the determination of total chromium and chromium(III) by electrothermal atomic absorption spectrometry was described by Beceiro-Gonzalez et al. [29]. Chromium(III) was chelated with 0.1 mol/1 quinolin-8-ol in methanol at pH 8 on heating, extracted with isobutyl methyl ketone and determined directly by GF-AAS. The complex was stable for at least 130 min, which was sufficient enough. The detection limit of this method was 12 ng/1, the recovery was ca. 90% for 200 ng/1 chromium added. The precision achieved for different amounts of chromium(III) was 2.8 ÷ 6.2%. Total chromium was determined by means of a preconcentration on the graphite tube using hot injection. The separation efficiency obtained for both species, calculated as the ratio of distribution coefficients of the two species, was nearly 1200. The authors did not give any results for the real water samples.

Another approach using the GF-AAS technique is chromium speciation described by Dungs et al. [30]. The differentiation of chromium(III) and chromium(VI) species becomes possible after reacting chromium(III) with trifluoracetylacetone inside the graphite furnace. A more recent version of this method applied to river water has been presented by Fung and Sham [31]. The working range of the method was 2 ÷ 300 µg/l chromium(VI) with the presence of up to 300 µg/l of chromium(III). The precision was found to be 3.8 ÷1.4% for 2.5 ÷ 25 µg/l chromium(VI).

A typical procedure for the determination of valency states of chromium using the coprecipitation method to separation and preconcentration of chromium species has been described in a paper [32]. The procedure is based on the direct co-precipitation with iron hydroxide prior to analysis by GF-AAS. It is well known that the hydrous iron(III) oxide is one of the most efficient co-precipitating agents. Its negatively charged colloids adsorb the chromium(III) species in sea water, while chromium(VI) is cop-

recipitated only to a negligible extent. Chromium(VI) is determined by the difference. In an independent sample chromium(VI) is reduced by Fe(II) hydroxide. The nascent Fe(III) hydroxide removes all dissolved chromium. The precipitates are separated from seawater solution, dissolved in hydrochloric acid and subjected to analysis by GF-AAS. The precision of the procedure is in the range of 5%. This has been achieved with ocean waters with total chromium concentration of about 150 ng/1. Lower precision must be expected for the analysis of chromium(III) species than for chromium(III) plus chromium(VI) only because of the considerably lower level in most natural sea waters.

A method described by Boughriet et al. [33] can be used for speciation analysis of chromium dissolved in seawater at considerably low concentration levels (30 ng/1 to 400 ng/1). This method is based on preconcentration by coprecipitation and electrothermal atomic absorption spectrometry. Chromium(III) was coprecipitated quantitatively and selectively with $Ga(OH)_3$ at pH 9.3 ÷ 9.5, then the precipitate thus obtained was dissolved with concentrated nitric acid and determined by ET-AAS. The percentage recovery was approximately 98% for chromium(III) and less than 1% for chromium(VI). It should be pointed out that the coprecipitation procedure with $Ga(OH)_3$ remains efficient for chromium(III), even in the presence of relatively high contents of soluble organic substances in sea water. Calibration was linear in the range of 0 ÷ 80 µg/l of dissolved chromium(III). The detection limit of the method was ca. 2 µg/l for chromium determination in preconcentrated solution, which corresponds to ca. 0.02 µg/l in the initial seawater sample. Total chromium [Cr(III) + Cr(VI)] was coprecipitated by a similar procedure after reducing chromium(VI) to chromium(III) with hydroxylammonium chloride.

Another approach has been proposed by Cox and McLeod [34]. Water samples immediately after collection, were passed through two microcolumns of activated alumina to isolate and retain chromium(III) and chromium(VI) species. The microcolumns of alumina were conditioned by drawing through 0.02 M nitric acid or 0.02 ammonium hydroxide; the acidic form of alumina has an affinity for anionic chromium species, the basic form of alumina has an affinity for cationic chromium species. The microcolumns were then incorporated into an on-line system and the species were eluted and quantified by ICP emission spectrometry. 2 M ammonium hydroxide was used to eluate chromium(VI) species and 2 M nitric acid to eluate chromium(III) species into the ICP. There is near perfect agreement between total chromium values and the sum of the chromium(III) and chromium(VI) data. The precision is sufficient, generally less than 2.5% RSD. The method has been tested successfully on surface waters containing 8 ÷ 20 µg/l chromium(III) and 1 ÷ 4.5 µg/l chromium(VI). The main advantage of this method is that the problems associated with stability of the samples can be avoided.

This author believes that this quite unique approach to speciation analysis can also be classified as semi-on-line flow injection ICP analysis.

Speciation Analysis in *on-line* Mode

On-line methods are those speciation analysis methods in which the whole sample pretreatment processes take place at a single run and within one analytical unit.

The on-line systems are automated, are more rapid, and, accordingly, are more likely to become the basis for routine determinations.

On-line methods are often applied by using flow injection analysis (FIA) techniques. The sample is injected into a carrier stream passing through a column which retains certain species. The carrier stream composition is changed and the species retained on the sorbents are directly eluted from the column into the detection systems, usually AAS or ICP-AES. Common sorbents include alumina, reverse phase materials, and various cation, anion or chelating resins.

One of the characteristics of flow injection is that this technique can work reproducibly under nonequilibrium conditions through the accurate control of time. This often results in a great reduction in the analysis time and allows the possibility of working reliably with unstable analyte species and reagents, e.g. chromium(VI) in acidic medium.

In most proposed on-line methods, one sorbent is used to preconcentrate and separate either chromium(III) or chromium(VI) in a single run. Sometimes the other species, which is unretained, is determined with an on-line detector, but with a poorer detection limit than the preconcentrated species. Alternatively, the concentration of the other species may be calculated by difference if the total chromium concentration is separately determined. This approach sometimes requires that the sample is first treated to convert all the chromium species to one oxidation state [41].

Such an approach allowing chromium(III)/(VI) speciation analysis in municipal wastes has been presented by Escobar et al. [36]. This method is based on the measurement of chromium(III)-catalyzed light emission from luminol oxidation by hydrogen peroxide. The apparatus consists of an FIA system with a flow cell suitable for chemiluminescence detection. Chromium(III) is determined directly by chemiluminescence. Chromium(VI) is reduced to chromium(III) by hydrogen peroxide in acidic medium and then the total amount of chromium is determined. The concentration of chromium(VI) is obtained by the difference between chromium(III) and chromium(VI) content. The method is simple, selective and rapid (tens of samples per hour). It requires a 0.4 ml injection volume of sample. The chemiluminescence intensity is linear from 0.01 µg/l up to 60 µg/l, the recovery range of chromium(VI) is from 91% to 110%, and RSD is 6%. In the presence of EDTA, most metal ions do not interfere with the determination of chromium(III). On the other hand, some organic compounds, which are present in waste water, could interfere with enhancing chemiluminescence, which must be considered in order to accurately determine chromium(III). This chemiluminescence intensity contributed by organic compounds has to have been determined previously, adding EDTA to mask cations including chromium(III). Also, organic compounds are destroyed during the treatment with H_2O_2 in an acid medium used for chromium(VI) reduction.

Sperling et al. [8] have developed a rapid and sensitive method for the species-selective determination of chromium(III) and chromium(VI) in water samples by flame atomic absorption spectrometry using on-line preconcentration on a microcolumn packed with activated alumina (acidic form). Sequential species-selective sorption is possible by using the Clark-Lubs buffer systems with pH 7 for chromium(III) and pH 2 for chromium(VI). Adsorption of chromium(III) decreases when competing cations are present because of the low selectivity of alumina. The

preconcentrated species are eluted directly from the column to the nebulizer-burner system using 1.0 mol/1 nitric acid and 0.5 mol/1 ammonia for chromium(III) and chromium(VI), respectively. The retention efficiency is higher than 80% for chromium(III) and higher than 90% for chromium(VI). The pretreatment method gives a sensitivity enhancement of 25 for a 3-ml sample loaded onto the column over 35 s. Satisfactory recovery of 90 ÷ 108% can be obtained from natural water samples. Linear calibration for both species is established over the concentration range of 10 ÷ 200 µg/l with detection limits of 1.0 and 0.8 µg/l for chromium(III) and chromium(VI), respectively.

Combining FI sorbent extraction preconcentration and separation on-line with ET-AAS has been shown to provide effective separation of the analyte from the matrix, low contamination, low sample and reagent consumption, high sample throughput and outstanding detection limits even in very complex samples. Chromium(VI) can be selectively determined by FI on-line solid sorbent preconcentration coupled with detection by ETAAS with a sensitivity and accuracy adequate for natural waters.

Sperling et al. [13] reported a method for the differential determination of chromium(III) and chromium(VI) in natural waters. In this method, chromium(VI) is preconcentrated selectively on a C_{18} bonded silica column using sodium diethyldithiocarbamate (NaDDTC) as the chelating agent, at pH 1.3 ÷ 1.8. The Cr-chelate is eluted with et-hanol into a special capillary, from which the most concentrated portion of 40 µl volume is transferred directly onto a platform of GF-AAS. The fact that nitric acid in this procedure is added on-line reduces the loss of chromium(VI), owing to a shift of the redox equilibrium to a minimum, because the sample is under acidic conditions for only about 0.5 s, which is an inherent advantage of FI techniques. Recovery of chromium(VI) from natural water is quantitative. Total chromium can be determined after off-line oxidation of chromium(III) to chromium(VI) by potassium peroxydisulfate. This solution has the advantage that the oxidation of chromium(III) will also include organically bound and colloidal chromium. The detection limit of this method (sample volume 3 ml) is : 16 ng/1 for chromium(VI) and 18 ng/1 for total chromium; precision for 121 ng/1 total chromium is 9.1%.

Determination of chromium in different oxidation states by selective on-line preconcentration on cellulose sorbents and flow-injection flame atomic absorption spectrometry has been described by Trojanowicz et al.[37]. The aim of their work was to examine the possibility of using commercial cellulose sorbents with various functional groups for the on-line preconcentration of chromium(III) and chromium(VI) in FI-FAAS. The effectiveness of Cellex P (dibasic phosphate ester of cellulose) and Cellex T (cellulose derivative with triethylamine functional groups) was investigated. Functionalized cellulose sorbents were found to be more appropriate for the on-line preconcentration of chromium(III) and chromium(VI) in a flow-injection system than conventional cation or anion exchangers or chelating resin. An advantage of the system was that both chromium(III) and chromium(VI) forms can be determined in the same aspirated sample volume without any sample pretreatment. The collected samples of surface water were filtered using a 0.45 µm membrane filter and acidified to pH 2.5 with HC1. Both chromium species were simultaneously preconcentrated on the Cellex T and Cellex P columns. The retained Cr(III) was eluted first by injection of 1 M HC1, then Cr(VI) was eluted by 1 M NaOH directly to the spectrometer without passing through the Cellex P column. For 50 ml of aspirated samples the detection limits were 0.78 and 1.4 µg/l for Cr(III) and Cr(VI), respectively. Using a 200-ml volume, three times lower values can be obtained. The precision achieved was 2.6% and 4.5% for 10 µg/l of each chromium species. As, in most cases, the concentration of both chromium forms in natural water samples was very close to the detection limit, all samples were spiked with 4.0 µg/l Cr(III) and 4.0 µg/l Cr(VI). The result was in moderate agreement with the total content of chromium found by ET AAS.

An automated two-column ion-exchange system for speciation of chromium in water samples has been developed by Sule and Ingle [35]. The system allows simultaneous preconcentration and determination of chromium(III) and chromium(VT) species in a single analytical cycle. The system is based on retention of cationic chromium(III) species by Chelex-100 resin and anionic chromium(VI) and negatively charged complexes of chromium(III) species (e.g. humic complexes) by AG MP-1 resin. The 0.01 M acetic buffer solution adjusted to pH 4.5 was used as the carrier stream solution. Maximum retention was observed between pH 4.0 and 4.5 for all subsequent experiments. The chromium species retained by the resins are eluted sequentially with stripping reagents (2.0 M HNO_3 and 2.0 M NH_4NO_3/O.5 M NH4OH, respectively) and are detected by an on-line flame atomic absorption spectrophotometer. The detection limit with a 2 ml sample loop is 2 µg/l for both species of chromium.

Chromatographic Methods

Chromatographic techniques are relatively seldom used in the speciation analysis of chromium. HPLC provides several advantages over many other methods, as the separation, the identification and the quantisation of the different species down to the trace concentration level can be performed in one procedure, but often results in inadequate sensitivity for trace concentrations of chromium in real samples of the most natural water because of low sample loading.

A method for the simultaneous determination of chromium(III) and chromium(VI) in water samples is described by Andrie and Broekaert [38]. Their method is based on the reaction of chromium(III) and chromium(VI) species with ammonium pyrrolidinedithiocarbamate (APDC). The reaction products are bis[N,N-pyrrolidine(dithiocarbamato-S,S')][N,N-pyrrolidine(dithioperoxycarbamato-O,S)]chromium(III) (Cr(VI) main product) and tris[N,N-pyrrolidine(dithiocarbamato-S,S')]chromium(III) (Cr(VI) - by-product); the last compound was formed also as a result of the reaction of chromium(IH) with APDC. The preparation procedure consists of three steps: complexation, extraction and preconcentration. A sample containing chromium(III) and chromium(VI) was treated by 0.2% APDC solution at pH 4.66 on heating. Then chromium complexes were extracted with ethyl acetate. After evaporating the solvent, the residue was dissolved in acetonitrile. The reaction products were again extracted with ethyl acetate and deter-

mined by reversed phase HPLC using UV-detection. The detection limits were 2.4 µg/l for chromium(III) and 2.1 µg/l for chromium(VI), calibration curves were linear between 5 µg/l and 5000 µg/l.

Several methods to determine the trivalent and hexavalent species of chromium in drinking water and groundwater by ion chromatography have been proposed by Dionex [39]. A method for rapid (5 min), routine speciation analysis of chromium at ppb levels utilizes a column reaction with a colour reagent. The chromium(III) is separated as a stable $Cr(PDCA)_2^-$ complex, while the hexavalent chromium, which does not form a complex with PDCA, is separated as the chromate ion. Because of the slow kinetics of ligand exchange for chromium(III), a pre-column derivatization with PDCA is used to form the $Cr(PDCA)_2^-$ complex in the samples. The pH values of the sample and eluent should be 6.8 to allow optimum separation and detection of both species. Greater values cause inhibition of the $Cr(PDCA)_2^-$ complex formation. In an acidic medium the chromate ions undergo a conversion to dichromate ions, which can be harmful to the column. After separation, the chromium(VI)-DPC complex is formed using postcolumn derivatization. The visible absorbances of the Cr(III)-pyridine dicarboxylic acid complex and the Cr(VI)-diphenylcarbohydrazide complex at 520 nm allow photometric detection of both species of chromium. Using injection volumes of 0.25 ml, determinations of chromium(IH) and chromium(VI) are possible to detection limits of 30 µg/l and 0.3 µg/l, respectively.

Coupled Techniques

Speciation has also been achieved by coupling different techniques such as FIA-AAS, FIA-ICP-AES, FIA-ICP-MS, HPLC-AAS, HPLC-ICP-AES, and HPLC-ICP-MS. In the last few years hyphenated techniques have been proposed also for on-line sample processing to chromium speciation analysis.

High-performance flow atomic spectrometry described by Berndt et al. [40] permits the fully automated separation and determination of chromium(III) and chromium(VI) species. In fact, the analytical setup is a typical combination of two techniques: HPLC and AAS. It has been built from commercial devices. In contrast to the commonly used coupling of HPLC with flame AAS, the exhaust of the HPLC column (modified Cm type) was not connected to a pneumatic nebulizer, but to hydraulic high-pressure nebulization (HHPN). Compared to pneumatic nebulization, a 4-times higher sensitivity was achieved in the determination of chromium. By the addition of tetrabutylammonium acetate to the sample as well as by using a water-methanol mixture as the carrier, both oxidation states could be on-line separated and measured within 60 s. If tetrabutylammonium acetate is added to the sample and water is used as the carrier, chromium(VI) is retained by the HPLC column, while chromium(III) passes the column (conditions for a preconcentration). Subsequently, chromium(VI) is eluted with a methanol-water solution. Methanol is added to the carrier in order to reduce the bonding strength. For chromatographic separation of real samples, TBAA should be added to the sample and 40% methanol should be used as a carrier. The detection limit is 0.03 µg/ml with respect to chromium(III) and 0.02 µg/ml with respect to chromium(VI). Samples of drinking water, samples of waste water and aqueous extracts of contaminated soil samples serve as matrices. The same type of chromium speciation column is also suitable for preconcentration of chromium(VI) traces. If the HPLC arrangement is extended by an additional, but not automatic valve, chromium(VI) can be determined within the lower microgram per liter range, and the detection limit is 0.5 µg/l. The relative standard deviation is 3.1 µg/l. Time for preconcentration and determination is only 3.5 min (drinking water).

A sensitive technique for analysis of chromium(III), chromium(VI), and total chromium has been developed using high-pressure liquid chromatography (HPLC) combined with direct injection nebulization (DIN) and inductively coupled plasma mass spectrometry (ICP-MS) [41]. Chromatographic separations were performed using Cetac microcolumn designated ANX1606-Cr. The column packing was a proprietary anion exchange resin. The column eluent, containing the nitrate anion, was adjusted to an acidic pH. The liquid sample and carrier were introduced to the column and ICP-MS via a gas displacement pump (GDP) and rotary valves. Two isotopes of chromium were individually used to determine detection limits. ^{52}Cr and ^{53}Cr produced detection limits for Cr(III) at 180 and 60 ng/1, respectively. Using ^{53}Cr, the Cr(VI) detection limit was 180 ng/1, and total chromium detection limits were determined to be 30 ng/1. ^{52}Cr was interfered by $^{36}Ar^{16}0$. This is the reason for the higher than normal background readings when monitoring a blank solution. ^{53}Cr also had oxide interferences, but to a much lower extent. The resultant short-term precision is 8%, 7% and 5% RSD for total chromium, chromium(III), and chromium(VI), respectively. Total chromium and chromium species were determined in one measurement with an analysis time of approximately 500 s. Accuracy measurements for the two chromium species were within 5% and recovery was also good (96% - **102%).**

Conclusions

As has been stated in the introduction, the methods of chromium speciation analysis are, to a large extent, limited by low concentrations of chromium species in water. The actual concentrations of dissolved chromium in natural water (several µg/l) reduce the number of useful analytical techniques to AAS, ICP, UV spectrophotometry, fluorimetry and ICP-MS. Atomic absorption spectrometry, both with flame and electrothermal atomization, is of the greatest importance. The AAS technique is specific in respect to chromium, but does not make it possible to determine its forms without initial separation of individual species. F-AAS cannot be used to determine individual species at desirable levels of concentrations as its sensitivity is too low. One of its unquestionable advantages is that it may be very easily coupled with other techniques. F-AAS is ideally suited for final determinations in on-line systems, particularly in flow injection analysis. Relatively small changes in the original software allow continuous recording of successive signals, which can be easily used to couple F-AAS with chromatographic techniques, e.g. HPLC. The GF-AAS technique is applied infrequently to on-line systems; nevertheless, due to its detection limits, it plays a significant role in the speciation analysis of chromium. The application of GF-AAS to chromium determination in AAS with atomization in a graphite furnace allows, in the tradi-

tional method of speciation analysis with preconcentration by coprecipitation, achievement of determination levels equivalent to those obtained by means of the most recent HPLC-ICP-MS coupled techniques. Analysis time is obviously beyond compare. While chromium speciation using the traditional method takes at least a few hours, the application of the coupled technique makes it possible to achieve the same result within a few minutes.

Acknowledgement

The author is grateful to prof, dr hab. inz. Jan R. Dojlido for his helpful comments and suggestions.

Support was provided by grant 6P04G03409 from the State Committee for Scientific Research (KBN).

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